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(54) Title of the Invention: **Polyester Elastomer Composition**

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SPECIFICATION**1. Title of the Invention**

Polyester Elastomer Composition

2. Claims

- (1) A polyester elastomer composition characterized by containing
- (a) 50-95 parts by weight of a polyester elastomer,
 - (b) 50-5 parts by weight of a copolymer with ethylene and vinyl acetate as the main repeating units, or a copolymer with ethylene and ethyl acrylate as the main repeating units,
 - (c) 2-40 parts by weight of a flame retardant, and
 - (d) 0.1-10 parts by weight of antioxidant.

(2) A polyester elastomer composition crosslinkable with ionizing radiation, obtained by adding (e) 0.1-10 parts by weight of a crosslinking auxiliary to the composition of Claim 1.

3. Detailed Description of the Invention

(Field of Industrial Utilization)

The present invention relates to a polyester elastomer composition that is suitable for coating insulated wire and the like, and that has excellent flame retardancy, resistance to heat deformation, thermal degradation resistance, and cut-through resistance.

In particular, the present invention relates to a polyester elastomer composition that has excellent properties such as flame retardancy and heat resistance, and does not allow the contained flame retardant or the like to bloom (bleed out).

(Prior Art)

The electrical wires used in locations such as the engine compartment of a high-performance automobile must have cut-through resistance at high temperatures.

Ordinary crosslinked polyethylene wires have low cut-through resistance at high temperatures because the melting point of polyethylene is 150°C or less. Wires with a tape made of a heat-resistant resin such as polyamide or polyethylene terephthalate (PET) wound around the inside of the insulating layer are used to resolve this problem.

Such a tape, however, complicates the production process and lacks reliability.

The present inventors developed heat-resistant wires by using a polyester elastomer that has an extremely high melting point (and hence excellent heat resistance) and possesses the requisite flexibility for use as a wire coating in the insulating layer to improve the cut-through resistance and resistance to heat deformation (Japanese Patent Application 1-18366).

This polyester elastomer contains 80-60% by weight of polybutylene terephthalate as the hard segment, and 20-40% by weight of an aliphatic polyester as the soft segment, and can yield

insulated wires with excellent heat resistance because the polyester elastomer has a melting point of 200°C or higher.

(Problems to Be Solved by the Invention)

However, the problem was that the flame retardant would bloom when this polyester elastomer was combined with decabromodiphenyl ether or another flame retardant to prepare a flame-retardant composition.

(Means Used to Solve the Above-Mentioned Problems)

The present inventors turned their attention to resins that have good compatibility with flame retardants, fillers, and the like, and perfected the present invention upon discovering that the flame retardant does not bloom (bleed out) from the composition when a copolymer with ethylene and vinyl acetate as the main repeating units (abbreviated simply hereinafter as EVA), or a copolymer with ethylene and ethyl acrylate as the main repeating units (abbreviated simply hereinafter as EEA) is used as a resin with good compatibility that is combined with a polyester elastomer.

Specifically, the present invention resides in the following.

- (1) A polyester elastomer composition characterized by containing
 - (a) 50-95 parts by weight of a polyester elastomer,
 - (b) 50-5 parts by weight of a copolymer with ethylene and vinyl acetate as the main repeating units, or a copolymer with ethylene and ethyl acrylate as the main repeating units,
 - (c) 2-40 parts by weight of a flame retardant, and
 - (d) 0.1-10 parts by weight of an antioxidant; and
- (2) A polyester elastomer composition crosslinkable with ionizing radiation, obtained by further adding (e) 0.1-10 parts by weight of a crosslinking auxiliary.

The present invention is explained greater detail below.

(1) An arbitrary polyester elastomer composed of a hard segment and a soft segment can be used as the polyester elastomer in the present invention.

Specific examples of polyester elastomers include polyester elastomers that have polybutylene terephthalate or another aromatic polyester as the hard segment, and an aliphatic polyester and/or aliphatic polyol as the soft segment. The ratio of the hard and soft segments is such that the melting point of the elastomer, which is an indicator of the heat resistance, is 200°C or higher; the weight ratio is within the range that does not detract from the resistance to thermal degradation or flexibility of the elastomer; and the weight ratio of the hard segment to the soft segment is 80:20-60:40.

Since thermal degradation tends to occur even with the addition of an antioxidant or the like when a polyol alone is used as the soft segment that constitutes the polyester elastomer, an aliphatic polyester resin with superior resistance to thermal degradation is preferably used, either singly or in combination.

(2) The following can be used as the EVA or EEA, which is added to prevent the blooming (bleed out) of the flame retardant, filler, and the like in the composition of the present invention.

(a) The EVA includes copolymers of ethylene and vinyl acetate, and also includes products in which these copolymers are copolymerized or graft copolymerized with another olefinic compound (such as vinyl chloride, (meth)acrylic acid and/or an ester thereof, maleic acid, or maleic anhydride), as well as partially or completely saponified ethylene-vinyl acetate copolymers.

Preferred examples of the EVA include ethylene-vinyl acetate copolymers, ethylene-vinyl acetate-maleic anhydride copolymers, partially saponified ethylene-vinyl acetate copolymers, and ethylene-vinyl acetate-maleic anhydride graft copolymers.

(b) The EEA includes copolymers of ethylene and ethyl acrylate, and also includes products in which these copolymers are copolymerized with a third olefinic compound (such as vinyl chloride, (meth)acrylic acid and/or an ester thereof, maleic acid, or maleic anhydride). It is especially preferable to use a copolymer of ethylene and ethyl acrylate.

The amount of ethyl acrylate copolymerized with ethylene need not be particularly restricted, but is preferably 2-35% by weight, and is more preferably 5-25% by weight.

(c) The amount of EVA or EEA added as a compatible resin is 50-5 parts by weight, preferably 40-10 parts by weight. The cut-through resistance of the composition at high temperature deteriorates and the advantages of using a polyester elastomer can no longer be ensured when the amount of compatible resin added exceeds 50 parts by weight because the melting point of these compatible resins is low at about 100°C. It becomes difficult to ensure the desired performance of the compatible resin, and the flame retardant blooms (bleeds out) when the amount added is less than 5 parts by weight.

(3) Arbitrary organic and/or inorganic flame retardants can be used to endow the polyester elastomer composition with flame retardance according to the present invention. It is preferable, however, to use organic flame retardants for wire coatings.

The following are specific examples of flame retardants that can be used.

(a) Halogen-containing organic compounds and phosphorus-containing compounds may be used as organic flame retardants. Specific examples of halogen-containing compounds include tetrabromobutane, perchloropentacyclodecane, tetrabromobisphenol A, chlorinated paraffin, brominated triphenyl phosphate, decabromodiphenyl, decabromodiphenyl oxide, and brominated epoxy. However, aromatic halogen compounds such as decabromodiphenyl are preferred from the standpoint of heat resistance.

(b) Examples of inorganic flame retardants include oxides and sulfides of antimony, arsenic, tin, and molybdenum, as well as hydroxides of aluminum and magnesium. Antimony trioxide is preferred.

(c) The amount of flame retardant used is within the range that does not harm the heat resistance, flexibility, and mechanical properties of the polyester elastomer and varies depending on the desired degree of flame retardancy. When used for wires and the like, it is preferably 2-40 parts by weight. Organic and inorganic flame retardants may be used individually or in combination depending on the goal.

(4) A polyfunctional compound must be added as a crosslinking auxiliary to make it possible to crosslink the elastomer composition of the present invention by means of ionizing radiation. This treatment makes it possible for the elastomer composition to retain its shape satisfactorily even under rigorous service conditions in which the temperature is 150°C or higher, sometimes 200-220°C, and can further improve the cut-through resistance. A wire coating material suitable for service temperatures of 150°C and higher in particular can be provided.

It also becomes difficult for the flame retardant to bloom (bleed out) because a reticular crosslinked structure is produced.

(a) Examples of this crosslinking auxiliary include 1,6-hexanediol dimethacrylate, trimethylolpropane trimethacrylate, pentaerythritol trimethacrylate, and other such methacrylic acid esters, as well as triallyl cyanurate and triallyl isocyanurate.

The amount of crosslinking auxiliary used is 0.1-10 parts by weight, preferably 0.5-5 parts by weight, per 100 parts by weight of the polyester elastomer. Adequate crosslinking does not occur when there is less than 0.1 parts by weight. More than 10 parts by weight lowers the strength of the polyester elastomer.

(b) The ionizing radiation used in the present invention includes γ -rays, electron beams, x-rays, ion beams, and neutron beams. γ -Rays and electron beams are advantageous for industrial utilization. The dose necessary for crosslinking varies depending on the type and amount of crosslinking auxiliary added, but is generally in the range of 1-30 Mrad.

(5) An appropriate amount of antioxidant must generally be combined in the polyester elastomer composition of the present invention because it tends to undergo thermal degradation, especially when it contains a polyol as a soft segment.

An arbitrary antioxidant can be used as the antioxidant of the present invention, and the appropriate antioxidant is preferably selected in accordance with the type of polyester elastomer used and the temperature of the environment in which the composition will be used.

The following compounds can be given as examples of antioxidants that are especially preferred for use in the present invention.

(a) Amine-based antioxidants: aromatic amine compounds such as 4,4'-bis(2,2'-dimethylbenzyl)diphenylamine and derivatives of 2,2,4-trimethyl-1,2-dihydroquinoline. However, 4,4'-bis(2,2'-dimethylbenzyl)diphenylamine is most preferred for its effectiveness in inhibiting thermal degradation.

(b) Hindered photostabilizers: Dimethyl-1-(2-hydroxyethyl)-4-hydroxy-2,2,6,6-tetramethylpiperidine succinate polycondensate, 2-(3,5-di-*t*-butyl-4-hydroxybenzyl)-2-*n*-butyl malonate bis(1,2,2,6,6-pentamethyl-4-piperidyl), and poly[[6-(1,1,3,3-tetramethylbutine)imino-1,3,5-triazine-2,4-diyl] [2,2,6,6-tetramethyl-4-piperidyl)imino]hexamethylene [[2,2,6,6-tetramethyl-4-piperidyl)imino]]. Among these, poly[[6-(1,1,3,3-tetramethylbutine)imino-1,3,5-triazine-2,4-diyl] [2,2,6,6-tetramethyl-4-piperidyl)imino]hexamethylene [[2,2,6,6-tetramethyl-4-piperidyl)imino]] is most preferred for its thermal degradation inhibiting effect.

A high thermal degradation inhibiting effect is also obtained by the joint use of an amino-based antioxidant and a hindered amine-based photostabilizer¹.

(6) UV absorbers, inorganic and/or organic fillers, foaming agents, lubricants, thermal stabilizers, colorants, and other additives may also be blended with the polyester elastomer composition of the present invention as needed.

It is appropriate to combine an inorganic filler with the polyester elastomer composition to ensure that flame retardancy lasts longer and there is no dripping. Examples of inorganic fillers include asbestos, talc, clay, mica, zinc borate, aluminum hydroxide, calcium carbonate, barium sulfate, and magnesium oxide. Talc, clay, and zinc borate are especially preferred.

(7) A single-screw extruder, multi-screw extruder, Banbury mixer, roll, kneader, heatable Henschel mixer, or other such high-speed fluidized mixer can be used in the production of the composition of the present invention. The composition can be produced by melt kneading the components at or above the melting point of the thermoplastic resin.

¹ Translator's note: Literally, "photo-inhibitor," which appears to be a typographical error.

The composition of the present invention is especially suitable as a wire coating material. It can also be used for purposes that require flame retardancy, such as in injection molded articles, tubes, extrusion molding, compression molding, roller molding, stretch molding, and foam molding.

(Operation of the Invention)

The polyester elastomer composition of the present invention has the following advantages.

(1) A resin composition in which the flame retardant does not bloom (bleed out) can be produced essentially by combining an ethylene-vinyl acetate-based copolymer or ethylene-ethyl acrylate-based copolymer as a compatibilizing resin with a flame retardant and filler.

(2) The polymer can be crosslinked and a three-dimensional reticular structure produced by incorporating a crosslinking auxiliary and applying ionizing radiation. This further improves the cut-through resistance at high temperatures. Furthermore, the three-dimensional reticular structure makes it difficult for the flame retardant to bloom (bleed out).

The present invention is described in greater detail below through working and comparative examples. These, however, do not limit the scope of the present invention.

(Working Examples)

Resin compositions with the mixture ratios shown by Working Examples 1-3 and Comparative Examples 1-3 in Table 1 were used to fashion insulated wires 0.4 mm in diameter.

The compositions were crosslinked by irradiation with electron beams, and the cut-through resistance, flame retardancy, and bloom (bleed out) of the coating layer were measured.

The results were as shown in Table 1.

As shown in Table 1, blending EVA or EEA with a polyester elastomer can produce a composition in which the flame retardant does not bloom (bleed out) and which has excellent cut-through resistance and flame retardancy.

In contrast to this, the flame retardant bloomed (bled out) when a polyester elastomer alone not blended with EVA or EEA was used.

The samples also failed the 150°C cut-through test when the amount in which EVA was added was 60% by weight.

Table 1

	Working Examples			Comparative Examples		
	1	2	3	1	2	3
Polyester elastomer ¹	80	70	60	100	40	100
EVA ²	20	—	40	—	60	—
EEA	—	30	—	—	—	—
Decabromodiphenyl ether	20	20	25	20	20	5
Antimony trioxide	5	5	10	5	5	5
Hindered amine-based photostabilizer	1	1	1	1	1	1
Amine-based antioxidant	2	2	2	2	2	2
Trimethylolpropane trimethacrylate	3	3	3	3	3	3
Electron beam dose (Mrad)	0	5	5	5	5	5
Cut-through resistance ⁴	Pass	Pass	Pass	Pass	Fail	Pass
VW-1	Pass	Pass	Pass	Pass	Pass	Fail
Bloom ⁵	No	No	No	Yes	No	Yes

¹: Polyester elastomer with a melting point of 202°C that contains aliphatic polyester as the soft segment

²: Vinyl acetate content = 15%, MI = 0.6

³: Ethyl acrylate content = 19%, MI = 5

⁴: CSA (CL1502) cut-through test at 150°C

⁵: Evaluated visually.

(Effect of the Invention)

The present invention provides a polyester elastomer composition which has good cut-through resistance at high temperature, in which the flame retardant does not bloom (bleed out), and which has excellent heat resistance and flame retardancy.